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STEP

AUTHORS: Zaykov, G.Ye., Mayzus, Z.K.

TITLE: Oxidation of methylethylketone in the liquid and gaseous phases

PERIODICAL: Kinetika i kataliz, v.3, no.6, 1962, 846-854

TEXT: A comparative study of the mechanism of oxidation of methylethylketone in the liquid and gaseous states was undertaken to elucidate the effect of polarity and the absence of hydrogen bonding in the oxidized molecules. The liquid phase oxidation was studied for the first time. Both the liquid and gaseous oxidation were carried out at 145°C and 50 atm. The liquid oxidation was a complex chain reaction imitating a first order reaction. Individual stages of the reactions were studied by adding  $\alpha$ -naphthol at various times during the reaction, this stopped the chain reactions and permitted to characterize the non-chain reactions. Diacetyl, ketohydroperoxide and ethylacetate (intermediate oxidation products) undergo non-chain decomposition, the hydroperoxide in this case decomposing much more rapidly than hydrocarbon hydroperoxides. Diacetyl decomposes

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at a higher rate than that calculated from the consumption of  $\alpha$ -naphthol which indicates that the branching reaction is not the only decomposition process. Ethylacetate is decomposed by water forming during the oxidation, acetic acid thus produced being a part of the total acid formed. The remainder of the acid is formed from the decomposition of diacetyl. Acetic acid is also formed from ketohydroperoxide via diacetyl. In the gaseous phase oxidation there is formation of formaldehyde, acetaldehyde, acetone, formic acid, methyl acetate, methyl alcohol and CO, which are not produced in the liquid phase oxidation. Conversely, the formation of ethylacetate and diacetyl decreases during the gaseous oxidation. There is little difference however in the formation of acetic acid. Comparing the rates of formation of the oxidation products during the two types of oxidation, the authors conclude that the specificity of the liquid phase oxidation is due to the polarity of the oxidized substance. Comparison with the oxidation of ethyl alcohol indicates that hydrogen bonds also affect the mechanism of oxidation. The mechanism of chain branching is the same for the liquid and gaseous oxidations which

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indicates that the polarity of the oxidized substance affects all the stages of the oxidation process. There are 6 figures and 2 tables.

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